



Carbon Nanotube Based Flexible Supercapacitors

by Christopher M. Anton and Matthew H. Ervin

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1. Background

Electrochemical double layer capacitors (Supercapacitors) are expected to play a significant role in future hybrid power systems due to their high specific power, cycle life, and tolerance of extreme environmental conditions (*1*). The development of flexible, conformable energy storage devices is also of great interest to the Army due to ease of packaging and coupling with flexible electronics. In supercapacitors, two electrodes are placed in an electrolyte and a voltage is applied between the two electrodes. During the application of voltage, an electrochemical double layer is formed on both electrodes when negative ions from the electrolyte are drawn to the positive electrode, and positive ions are drawn to the negative electrode. When these ions are released by opening a path between the positive and negative electrodes, the energy stored in the double layers is discharged through the external circuit.

Because supercapacitors store charge only on the electrode surfaces, maximizing the amount of surface area that is accessible to the electrolyte ions is of critical importance. Conventional supercapacitors typically use activated carbon electrodes on top of a current collector. Carbon is an excellent electrode material due to a variety of favorable chemical properties, including chemical stability and large electrochemical windows in a variety of electrolytes (*1*). The advantage of activated carbon is its low cost relative to competing electrode materials. The disadvantage is its modest specific capacitance (capacitance per mass), due to the fact that electrolyte ions cannot collect between the individual graphene layers of the activated carbon electrode.

Carbon nanotube (CNT) electrodes have been thoroughly investigated as supercapacitor electrodes over the past decade. CNTs are an appealing electrode material due to their high conductivity, and the fact that single walled carbon nanotubes (SWCNTs) are comprised entirely of surface atoms that could interact with electrolyte ions. Another advantage of CNT electrodes is their ability to bend and flex. Activated carbon electrodes typically require binders and conduction additives that do not contribute to overall device capacitance and add weight to the system. CNT electrodes do not typically require any type of binder. Several different methodologies have emerged in the literature to fabricate flexible CNT based supercapacitor electrodes. CNTs have been spin coated (*2, 3*), filter deposited (*4*), spray deposited (*5*), or directly grown through chemical vapor deposition (*6–8*) onto a variety of flexible substrates including plastics and carbon cloth. More recently, CNTs suspended with sodium dodecylbenzenesulfonate (SDBS) surfactant have been deposited directly onto paper to form a porous, conductive CNT electrode (*9–10*). Hu et al., were able to show a ~3X increase in specific capacitance when they compared CNT films deposited onto Xerox paper substrates to CNT films deposited onto PET plastic substrates (*9*). This technique was selected as a starting

point for our supercapacitor electrode fabrication due to its apparent performance advantage when compared to other published techniques.

2. CNT Supercapacitor Electrode Fabrication and Testing

In order to realize a packaged flexible supercapacitor, it was necessary to develop an electrode fabrication technique. Standard copier paper was chosen as a substrate, and a variety of CNT suspensions were deposited onto the substrate by drop casting. A hot plate was used to heat 1 cm^2 substrates, which sped up the drop casting process by aiding in solution evaporation. Hot plate temperatures ranged from $80\text{ }^{\circ}\text{C}$ to $150\text{ }^{\circ}\text{C}$ depending on the CNT solution being deposited. Typically, $25\text{ }\mu\text{l}$ of CNT solution was placed on the substrate and allowed to sit until the paper dried. The process was repeated until the desired CNT solution volume was deposited onto the paper.

CNT/paper electrodes were evaluated both by their CNT film morphology and their electrochemical performance as supercapacitor electrodes. CNT film morphology was analyzed using an FEI Quanta environmental scanning electron microscope (ESEM). After CNT deposition was complete, electrodes were evaluated in the ESEM without further preparation. Following ESEM analysis, the electrodes were prepared for electrochemical analysis by clamping one edge of the electrode with nickel foil in order to provide an inert connection to the measurement apparatus (figure 1). A second piece of Ni foil was used to clamp the electrode to an acrylic plate, allowing the entire electrode to be submerged in a liquid electrolyte for testing.

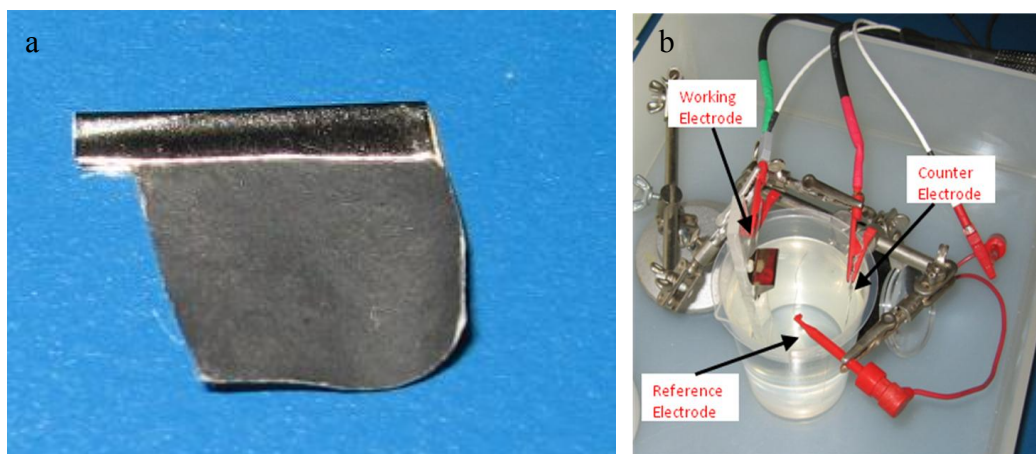


Figure 1. (a) CNT/paper electrode with an attached Ni foil clamp to provide good electrical contact to the CNT film. (b) Electrochemical half cell experimental setup.

Individual electrodes were tested in a half cell configuration using a Princeton Applied Research Versastat 3, in which the CNT/paper electrode was the working electrode and a piece of Ni foil was the counter electrode. A Warner Instruments Ag/AgCl pellet electrode was used as the

reference electrode. The three electrodes were submerged in a beaker of 1M KOH solution. Ni foil was used in these experiments because it has a useful electrochemical window in KOH. In order to obtain capacitance values for each electrode, cyclic voltammetry was performed. The measurements were made under realistic conditions so that measured capacitances reflected practically usable values. A review of the literature by Istvan has revealed that changing the cyclic voltammograms (CV) scan rate from 5 to 20 mV/s, or the galvanostatic charge/discharge current from 10 to 200 mA/g, will reduce the measured capacitance by 20% (11). Therefore, standard test conditions of 20 mV/s and 200 mA/g or higher were used for all experiments. Devices were cycled five or more times before analyzing the CV curves in order to exhaust any irreversible redox contributions to the capacitance due to impurities that would exaggerate the measured capacitance. Electrode capacitance was calculated by dividing one half of the gap between the charge current and the discharge current by the scan rate, and dividing this current value by the scan rate. This measurement was made at a voltage location where no redox peaks were present. We then divided this number by the total CNT mass deposited onto the electrode in grams, yielding specific capacitance. The CNT mass was calculated by multiplying the volume of solution deposited and the CNT solution density.

2.1 Impact of CNT Solution on Performance

We discovered early in this work that the CNT solution used to fabricate the supercapacitor electrode played a critical role in its performance. Initial efforts focused on investigating the impact that the CNT solution had on the resulting CNT film morphology and electrode electrochemical performance. The commercially obtained CNT solutions, except for sample 4 described in table 1, were drop cast onto 1 cm² paper substrates. Samples 1–3 were fabricated using SWCNTs with different functional groups on the CNT surface. These three solutions also contained dispersants from the manufacturer that allowed for a greater concentration of CNTs to be suspended in the solutions. We made the solution used to fabricate sample 4 by suspending 15 mg of CVD grown SWCNT powder in a 10 mg/ml solution of SDBS in deionized water. The solution was then bath sonicated for 5 min, followed by 30 min of probe sonication to help disperse the CNT powder in the surfactant solution. A previous study of CNT/surfactant suspensions in water has shown that SDBS is the most effective surfactant for suspending high density CNT solutions (12). SDBS was also the solution used by Hu et al., to successfully fabricate CNT/paper electrodes with specific capacitance values approaching 200 F/g (9). The fifth sample was fabricated using a commercially purchased low density solution of COOH functionalized SWCNTs suspended in water without the use of surfactants.

Table 1. Impact of initial CNT solution on CNT/paper electrode performance.

Sample	CNT type	Solution	Volume Deposited/ CNT mass Deposited	Resistance	Specific Capacitance
1	COOH SWCNT	acetone	1 ml/0.4 mg	200–2000 Ohm	3.75 F/g
2	Aminopyrene SWCNT	acetone	1 ml/0.4 mg	Not conductive	0 F/g
3	Pristine SWCNT	acetone	1 ml/0.4 mg	80k–400k Ohm	0.25 F/g
4	CVD SWCNT powder	SDBS	0.267 ml/0.4 mg	200–1000 Ohm	13.75 F/g
5	COOH SWCNT	water	2 ml/0.1 mg	150–200 Ohm	91.25 F/g

The mass of CNTs deposited onto the paper substrate was calculated based on the volume of solution drop cast onto the substrate and the CNT density of the various solutions. Initially, the paper electrodes were weighed before and after CNT deposition. However, because of variations in the water content of the paper substrate, it was impossible to obtain an accurate measurement of the deposited CNT mass. The densities of the CNT solutions were confirmed by dispensing a known volume of CNT solution onto an aluminum foil sheet and weighing the sheet before and after deposition.

The resistance values of the CNT films covering the paper substrates were measured using a digital ohmmeter. The paper was probed repeatedly at different locations, which is why a range of resistance values appears. This is not intended to be a quantitative measure of the true sheet resistance of each electrode, but rather a comparative measure between the five samples above. Specific capacitance values were calculated from cyclic voltammetry measurements described above. 1M KOH was used as the liquid electrolyte, and scan rates of 20 mV/s were used for all five sample measurements.

As can be seen in table 1, the specific capacitance values achieved by the five electrode samples vary widely. The surfactant-free COOH SWCNTs in water clearly outperform the other CNT solutions, reaching a specific capacitance of 91.25 F/g. This value is on par with the best CNT supercapacitor electrodes that do not use pseudocapacitive materials. We believe that the surfactants and dispersants that are used to suspend the CNTs in the other solutions are having a detrimental effect on the electrode performance. This theory is supported by the CNT film morphologies observed under ESEM analysis in figure 2, where CNT bundling and contamination are clearly present in samples 1 and 4. CNT bundling was also observed in sample 5, but the severity of the bundling was clearly less than the other samples. There were also no signs of the additional contamination that was observed in samples 1 and 4. Samples 2 and 3 (not shown) also contained CNT film contamination similar to samples 1 and 4. It is likely that the open pore structure seen in sample 5 allows electrolyte ions to more completely penetrate the CNT film, resulting in higher specific capacitance.

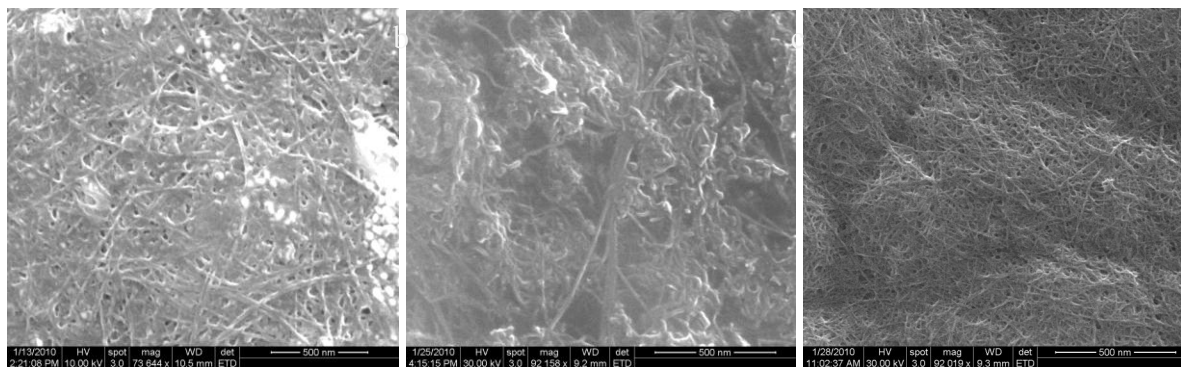


Figure 2. ESEM images of COOH SWCNTs suspended in acetone (a) (sample 1), SWCNTs in SDBS/diH₂O (b) (sample 4), and COOH SWCNTs in H₂O (c) (sample 5), deposited on paper substrates. Scale bars = 500 nm.

2.2 Impact of Surfactant on Performance

The use of surfactants and dispersants in the CNT solutions appear to have a negative impact on the overall device performance, resulting in excessive CNT contamination. We were unable to achieve the ~200 F/g specific capacitance described by Hu et al., using their SWCNT/SDBS solution protocol (9). It is possible that differences in the starting CNT materials resulted in the differences in specific capacitance seen between sample 4, 5, and Hu's work. In order to confirm the impact of SDBS surfactant on electrode performance, a new CNT solution was made. 10 mg SDBS powder was mixed with 2 ml of the COOH SWCNT in water suspension used to fabricate sample 5. This eliminated the variability between nanotubes used, and should provide an accurate measure of the impact of having SDBS surfactant present in the CNT solution. Sample 8 was made by drop casting 2 ml of the new solution onto a paper substrate.

CNT film morphology was clearly impacted by the addition of the SDBS surfactant to the COOH SWCNT/water solution. The CNT film porosity has been visibly degraded, leading to reductions in the discharge current of the CV plots in figure 3. Table 2 shows a 10X reduction in specific capacitance due to the surfactant addition, with a large increase in resistance compared to sample 5. This indicates that the CNT conducting network is degraded, and the surface area available for the electrolyte ions to access has been reduced.

After device testing was complete, sample 8 was soaked in a deionized water bath for 30 min in an attempt to wash away unwanted surfactant molecules. We then loaded the sample into a furnace and heated to 180 °C for 2.5 hr. Additional device testing was performed, and the results are shown in table 2 under sample 8*. The washing and heat treatment did improve the electrode performance, most likely by driving off some of the surfactant, but electrode performance was still 3X below the sample that did not contain surfactant. Further rinsing and heat treatments did not improve device performance. The results of this study indicate that surfactants should be avoided in order to preserve CNT film porosity and to maximize electrode conductance and capacitance.

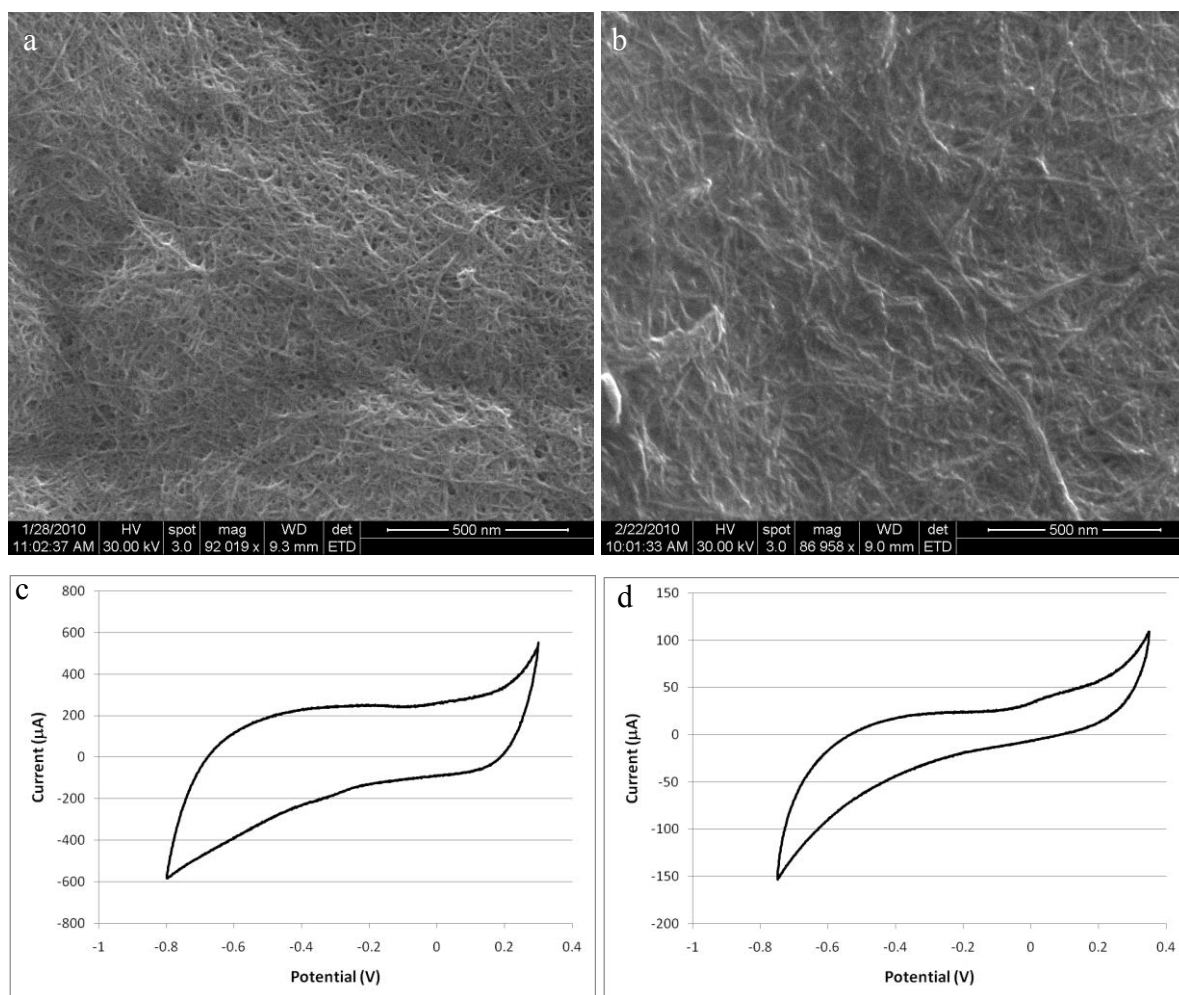


Figure 3. CNT film morphology and CV plots of SWCNT supercapacitor electrodes both with and without SDBS surfactant. ESEM images show (a) sample 5 with no SDBS, and (b) sample 8 with SDBS. CVs were taken at a scan rate of 20 mV/s and a scan range of -0.7 V to $+0.3$ V for both (c) sample 5, and (d) sample 8. ESEM scale bars = 500 nm

Table 2. Comparison of electrodes fabricated with and without SDBS surfactant. Sample 8* has undergone rinsing and heat treatment to remove unwanted surfactant molecules.

Sample	CNT type	Solvent	Volume Deposited/ CNT mass Deposited	Resistance	Specific Capacitance
5	COOH SWCNT	water	2 ml/0.1 mg	150–200 Ohm	91.25 F/g
8	COOH SWCNT	SDBS	2 ml/0.1 mg	50–200 kOhm	10.9 F/g
8*	COOH SWCNT	SDBS	2 ml/0.1 mg	0.8–1.5 kOhm	28.8 F/g

2.3 CNT Mass Loading Study

In order to ascertain if the entire CNT film was being accessed by the electrolyte, we performed a mass loading study. Three electrodes (samples 5–7) were fabricated using COOH SWCNTs in water, as described in table 3. The only variable changed in this experiment was the volume of CNT solution that was deposited onto the paper substrates. If the electrolyte is not able to

penetrate the CNT film, the specific capacitance would be reduced by roughly 50% for each doubling of overall CNT mass because the added mass would not increase the overall capacitance of the electrode.

CVs, shown in figure 4, were captured for all three samples under the same experimental conditions. Again, 1M KOH was used as the electrolyte, and a scan rate of 20 mV/s was used to generate the plots. A scan range of -0.8 V to $+0.3$ V was used for all three scans. The roughly rectangular shape of the CV plots is indicative of capacitive charge storage.

As seen in table 3, no clear trend in specific capacitance was observed when the CNT mass loading was increased. The differences in specific capacitance between the three samples may have been due to variabilities in the drop casting process, which is done by hand and does not ensure consistent CNT film coverage across the entire substrate. However, it is clear that the liquid electrolyte is able to penetrate the varying thicknesses of the CNT films of samples 6–8. If this was not the case, a clear downward trend in specific capacitance would have been observed.

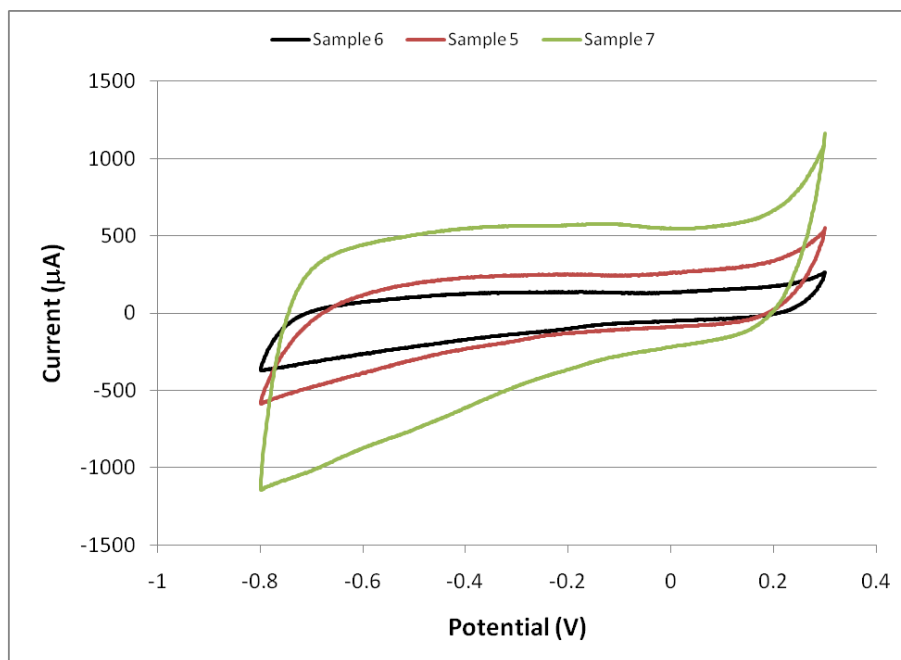


Figure 4. Cyclic voltammograms of sample 5, sample 6, and sample 7 using a 20 mV/s scan rate.

Table 3. Impact of mass loading on CNT/paper electrode performance.

Sample	CNT type	Solvent	Deposited Volume/ CNT mass Deposited	Resistance	Specific Capacitance
6	COOH SWCNT	water	1 ml/0.05 mg	100–300 Ohm	101.5 F/g
5	COOH SWCNT	water	2 ml/0.1 mg	150–200 Ohm	91.25 F/g
7	COOH SWCNT	water	4 ml/0.2 mg	80–160 Ohm	115.6 F/g

2.4 MWCNT Electrodes

In addition to SWCNT electrodes, several multi-walled CNT (MWCNT) electrodes were made. It is expected that the specific capacitance of MWCNT electrodes would be less than a comparable electrode made using SWCNTs because the electrolyte ions cannot access the inner shells of the MWCNTs. This means that the inner tubes of a MWCNT would add weight to the electrode without providing any additional capacitance. MWCNT electrodes were expected to be more conductive due to the fact that MWCNTs are metallic, whereas SWCNT solutions contain a mixture of semiconducting and metallic CNTs. A commercially available MWCNT suspension in water with no added surfactants or dispersants was used to fabricate the MWCNT/paper electrodes. 1 ml of 0.05 mg/ml MWCNT solution was drop cast onto a paper substrate that was placed on a 150 °C hot plate. The sample was then imaged, and finally tested in the electrochemical half cell measurement setup with the results shown in figure 5.

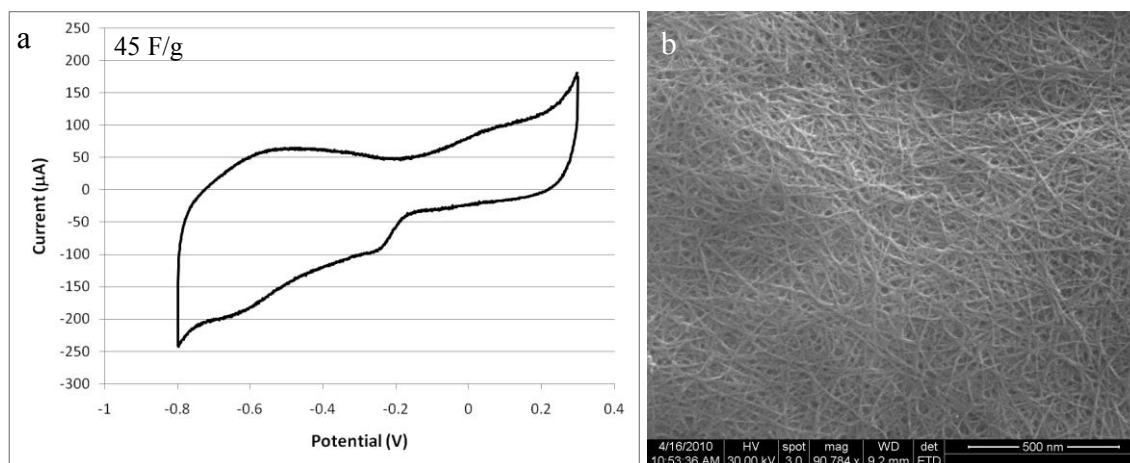


Figure 5. CV (a) and ESEM image (b) of a MWCNT/paper supercapacitor electrode.
ESEM scale bar = 500 nm

The electrode CNT morphology appears similar to the SWCNT electrodes. An open pore structure is maintained and no obvious signs of contamination are present. The electrode had a specific capacitance of 45 F/g, roughly half of the capacitance of a SWCNT electrode. The CV plot does show several peaks that are more pronounced than observed in the SWCNT electrodes. These may be due to surface groups on the MWCNTs that were not present on the SWCNT devices. The specific capacitance of this electrode was evaluated at a potential on the CV plot that was free of obvious redox peaks that could confuse the results (-0.15V was used for this electrode). We observed a resistance of 50–150 ohms which is lower than the typical SWCNT electrode.

3. CNT Flexible Supercapacitor Device Assembly

Following the CNT/paper electrode development work, we considered the issue of electrolyte selection and packaging. Liquid electrolytes are advantageous for many systems due to their superior ion mobility when compared to solid or gel electrolytes. However, liquid electrolytes are more prone to leaking when used in a flexible device. Electrolyte leakage not only compromises the functionality of the device, but could cause damage to its surrounding environment. In order to address these shortcomings, the performance of liquid KOH electrolytes was compared to a PVA:KOH gel electrolyte.

For liquid KOH supercapacitors, a 1M KOH solution was used. The PVA:KOH gel electrolyte was prepared in a ratio of 3:1 PVA to KOH (13). To begin, a 70 mg/ml solution of PVA in deionized water was made. The solution was heated to a temperature of 130 °C and stirred continuously until the liquid turned from opaque to clear. Following the solution clearing, the appropriate amount of 1M KOH was added and allowed to mix for 5 min to achieve the proper ratio. The PVA:KOH solution was then poured into PTFE dishes and allowed to dry into a moist gel. The result is a very robust opaque white elastomeric gel. Care must be taken not to allow the gels to dry completely, as they lose flexibility as well as their ability to perform as an electrolyte.

The material chosen to encase the electrodes and electrolyte was a flexible polyester film. The film was sealed using a thermal sealer to melt the polyester together and form a pouch that encapsulates the device. The film did not degrade in the presence of KOH. Assembling full devices also required a new method for making electrical contact with the electrodes. To accomplish this, the same Ni foil clip was applied to one edge of the electrode. A thin Ni wire was then tack welded to the Ni foil clip. This provided good electrical contact, and also allowed the polyester pouch to be sealed around the thin wire to limit electrolyte leakage.

Three packaged supercapacitor structures were fabricated and compared, and are represented schematically in figure 6. The liquid KOH electrolyte architecture used 1M KOH as the electrolyte. Two CNT/paper electrodes were arranged so that the CNT films were facing each other. The two electrodes were separated by a third piece of plain copy paper that had been soaked in the KOH solution. The stack was assembled in a polyester pouch, which was then thermally sealed around the device. The gel electrolyte sandwich architecture used a PVA:KOH gel electrolyte. Again, two CNT/paper electrodes were assembled facing each other. A piece of PVA:KOH gel was cut to the appropriate size and placed between the two electrodes. This gel served as both the electrolyte and the separator that prevented electrode shorting. Again, the electrode/electrolyte stack was sealed in a polyester casing. The cast gel electrolyte architecture involved casting the electrolyte gel over and around CNT/paper electrodes, encapsulating the individual electrodes. This was done by placing each electrode in a small dish, and pouring hot

liquid PVA:KOH solution over the electrodes. The gel was allowed to form, encapsulating the electrodes. Two gel encapsulated electrodes were then sandwiched together without any separator, and sealed in the package. We hypothesized that the gel casting process would allow the gel electrolyte to more completely penetrate the CNT film, proving superior capacitance and increased performance stability under bending when compared to the gel sandwich structure.

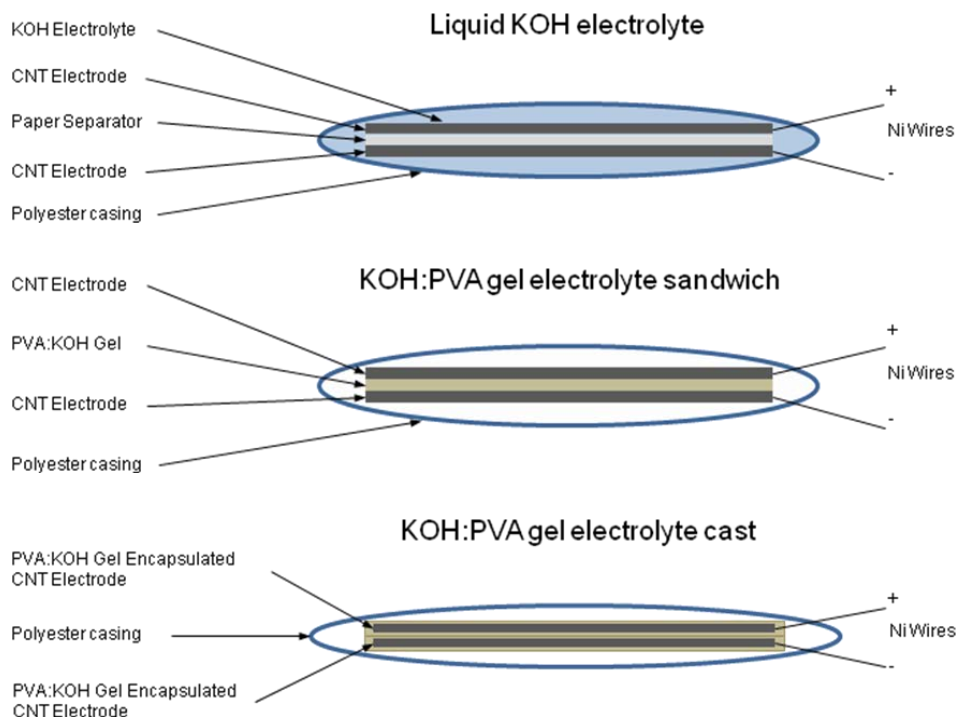


Figure 6. Full cell packaged flexible supercapacitor architectures.

One additional issue that arose when assembling the packaged supercapacitors was non-flat CNT/paper electrodes. During CNT deposition, it was common for the paper to become wrinkled due to the repeated wetting and drying that it was subjected to. This became a problem when assembling packaged devices. It also made casting electrodes in the gel electrolyte very difficult because it was necessary to completely cover the electrodes with the gel in order to prevent device shorting. To address these issues, the CNT/paper electrodes were flattened prior to being fitted with the Ni clips and assembled. The electrodes were first soaked in deionized water for 1 min to wet the substrates. The electrodes were removed from the water bath and sandwiched between a piece of absorbent cleanroom paper and a thick glass microscope slide. A small amount of weight was placed on top of the glass slide, forcing the paper completely flat. The electrodes were left in this configuration for several hours until the substrates were dry. This method was successful in producing very flat CNT/paper electrodes, which made device assembly much easier.

4. CNT Flexible Supercapacitor Device Testing

Device testing began by constructing three packaged devices. One of each device configuration described above was constructed using MWCNT/paper electrodes as described in section 2.4. Assembled devices were tested in a full cell configuration. All CVs were taken at 20 mV/s scan rates. Note that an assembled full cell supercapacitor is actually two capacitors in series, where the total capacitance $C_t = (C_1 \times C_2) / (C_1 + C_2)$. The devices were tested both flat and under static bending with the results shown in figure 7. Static bend tests were performed by wrapping the packaged devices around mandrels of varying diameters and taking CV measurements under each bending condition. We used rubber bands to secure the supercapacitors to the mandrels. A pressure test was also conducted on each device, where a small amount of weight was placed on top of the supercapacitor package, and CV measurements was taken under this condition.

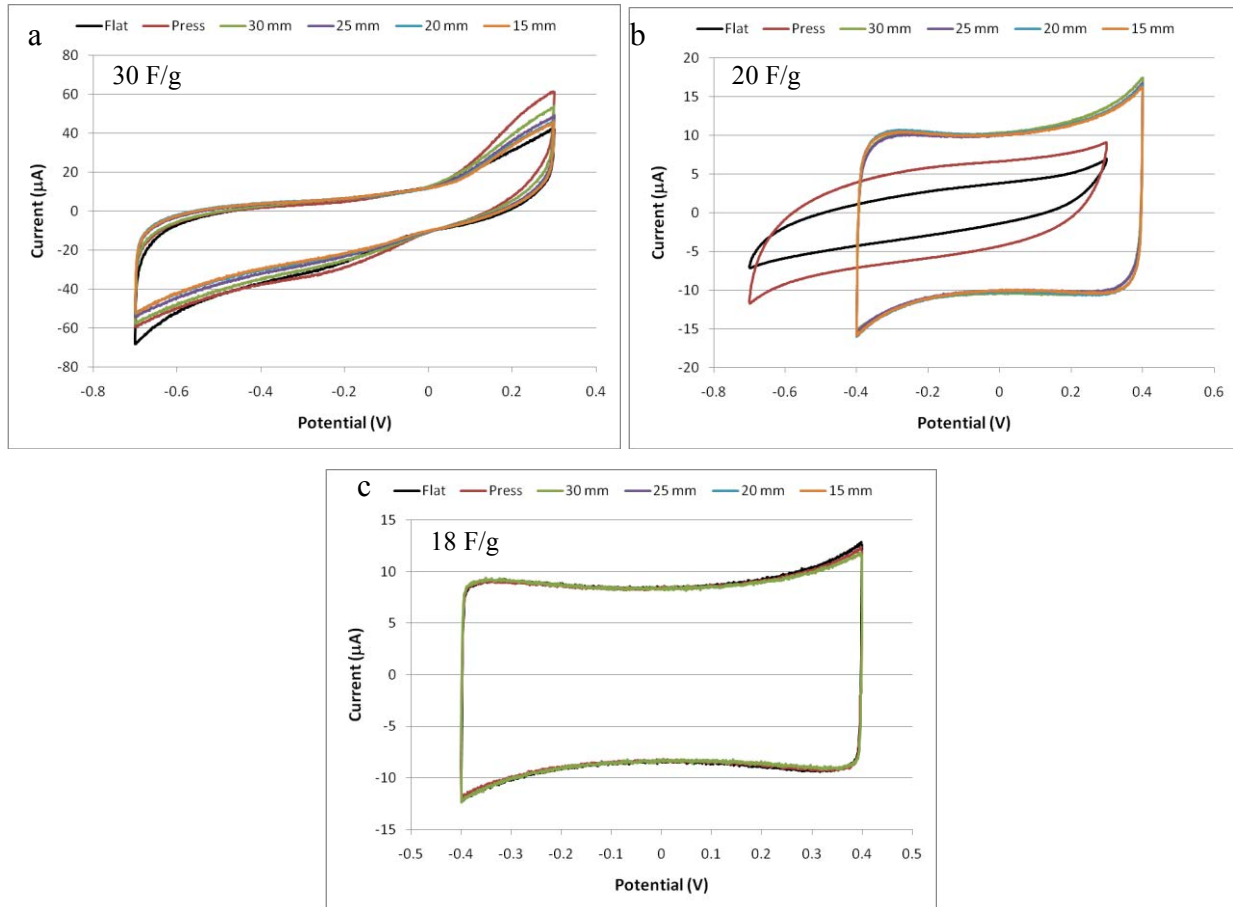


Figure 7. Cyclic voltammograms of (a) Liquid KOH electrolyte packaged supercapacitor, (b) PVA:KOH gel sandwich packaged supercapacitor, and (c) PVA:KOH cast gel packaged supercapacitor under varying states of bending.

The liquid electrolyte device showed the best energy storage performance, with a specific capacitance of 30 F/g. This was expected, as the KOH ions are much more mobile in the liquid than they are in the gel matrix. There was some variability as the bending conditions were changed, but no appreciable trend was observed. The gel sandwich supercapacitor showed greater performance variability due to the loading conditions on the device. The flat or unloaded test showed very little capacitance. Applying pressure to the device increased the capacitance, as did the bend tests. No appreciable variability was observed between the four different bend diameters. It is believed that the pressure applied during the pressure and bending tests forced the PVA:KOH gel electrolyte into more intimate contact with the electrodes, improving ion intercalation and energy storage. It is also possible that liquid KOH is released from the gel during bending, which wet the electrodes and improved device performance. The gel cast supercapacitor showed the lowest specific capacitance (18 F/g), but showed no sensitivity to its loading conditions. The lower capacitance observed in the gel cast supercapacitor may be due to PVA molecules occupying some of the CNT surface area, making them inaccessible to KOH ions.

5. Conclusions

Flexible packaged supercapacitor devices have been successfully fabricated and tested. Electrode fabrication studies showed a strong correlation between CNT film cleanliness and electrode performance. Dispersant agents used to suspend CNTs in solution proved detrimental to electrode performance, resulting in low specific capacitance values. Electrodes fabricated using commercially available dispersant-free CNT suspensions in water from Brewer Scientific proved to produce the best performing CNT/paper electrodes, with specific capacitance values in excess of 100 F/g.

Flexible full cell capacitors were produced in three different configurations. Each packaged device architecture produced unique device performance. The liquid electrolyte device produced the highest specific capacitance, but the possibility of electrolyte leakage is a major disadvantage of this device design. The gel sandwich supercapacitor showed the second best device performance under bending, but its performance was variable under different bending conditions. This variability is undesirable, as it would introduce changes in energy storage capability under different system loading conditions. The gel cast supercapacitor had the lowest specific capacitance of the three assembled devices. However, the fact that device performance did not vary under any of the bending conditions, coupled with the low likelihood of electrolyte leakage when compared to a liquid electrolyte device, makes the gel cast device architecture attractive despite the performance penalty.

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List of Symbols, Abbreviations, and Acronyms

CNT	carbon nanotube
CVs	cyclic voltammograms
ESEM	environmental scanning electron microscope
MWCNT	multi-walled CNT
SDBS	sodium dodecylbenzenesulfonate
SWCNTs	single walled carbon nanotubes

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